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A review of the bioactivity and flavor properties of the exotic spice "andaliman" (*Zanthoxylum acanthopodium* DC.)

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ABSTRACT

Andaliman (*Zanthoxylum acanthopodium* DC.) is a plant endemic to North Sumatera, Indonesia. It has been used as food ingredient because of its unique properties of its pericarp, such as its citrus-like aroma, warm peppery flavor, and its ability to induce a tingling sensation. However, the pericarp is easily degraded by environmental and processing conditions. Therefore, preservation techniques, such as encapsulation and drying, have been proposed to protect the flavor. Moreover, andaliman also has some potential biological activities related to its antimicrobial, antioxidant, and anti-inflammatory properties. Thus, this plant may have many health benefits and uses. This review discusses the flavor profiles and bioactive compounds of andaliman, in addition to its applications in the food industry as a flavoring ingredient.

KEYWORDS

Andaliman; bioactive compounds; flavour; preservation technology; *Zanthoxylum acanthopodium* DC.

Introduction

Indonesia is well known for its diversity of herbs and spices, especially for the ethnic ones. These include betel nut in Papua, nutmeg and cloves in Moluccas, kecombrang in East Nusa Tenggara, onion in Borneo, and various types of shallot and rhizomes (such as galangal, java turmeric, and ginger) in Java. These spices confer distinctive flavors to foods and may provide health benefits as well.

Andaliman (*Zanthoxylum acanthopodium*) is a wild plant that grows well in North Sumatera in Indonesia. It has been utilized by the Batak people (an ethnic group in the northern part of Sumatera) for centuries as an important flavoring ingredient in Batak cuisines, such as arsik (cooked golden fish), tombur (a condiment used with grilled fish), naniura (uncooked or fermented goldfish), and napinadar (fish or grilled meat).[1] Andaliman has a specific citrus-like aroma and induces a strong tingling sensation on the tongue, which makes it unique.

The *Zanthoxylum* genus belongs to the Rutaceae family. Plants in this genus are mainly utilized as spices and medicinal agents. The name *Zanthoxylum* was coined in 1757 by Linnaeus. The genus contains over 546 species from around the world. Of these, 250 species are distributed in tropical and temperate regions of Asia and North America. *Zanthoxylum* is a dioecious plant. Some are shrubs, while others are trees that can grow up to 20 m high. The plants are usually identified by their prickly branches or trunks (Fig. 1).[2–4] The fruits are aromatic aggregates of modified follicles or pericarp. Each fruit has a single shiny black seed (Fig. 2).[2,3,5]

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Figure 1. Prickly branch and trunks of *Zanthoxylum* species (A) *Z. clava-herculis*, (B) *Z. americanum*, (C) *Z. alatum*, and (D) *Z. acanthopodium* DC.

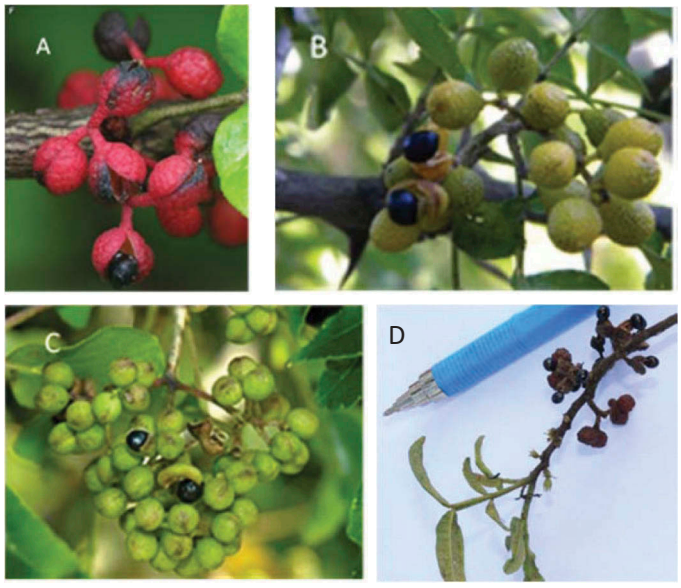

Figure 2. Fruit and seeds of *Zanthoxylum* species: (A) *Z. americanum*, (B) *Z. capense*, (C) Z. *clava-herculis*, and (D) *Z. acanthopodium* DC.

Members of *Zanthoxylum* have been used as traditional spices, including *Zanthoxylum piperitum* (Japan), *Zanthoxylum schinifolium* (Korea), *Zanthoxylum simulans* (Taiwan), and *Zanthoxylum rhetsa* (India). However, the genus *Zanthoxylum* is not only used as a spice, but it is

also used in folk medicine in parts of Asia and North America (Table 1). Almost every part of the plant has its own function. The pericarp and the leaves of *Z. piperitum*, which grows in Japan, Korea, and China, are usually used as daily spices. Meanwhile, the wood and bark of *Z. americanum* can be used as healing ingredients for problems, such as bronchial disease, congestion, burns, cough, itchy skin, pulmonary trouble, ulcerated throat, wounds, and skin sores.[6]

Zanthoxylum plants, such as *Z. simulans* (Chinese red pepper) and *Z. piperitum* (sansho, a spice from Japan), are well known as natural flavors that cause unique sensations in the mouth upon ingestion. *Z. acanthopodium*, one of the genera found in Indonesia, has been shown to contain similar compounds as those found in *Z. piperitum*.[7]

The use of spices as food additives has been in practice for centuries. Spices are added not only to enhance the aroma and taste of food but also to provide health benefits. In addition to its unique flavor, recent studies have shown various biological activities of this spice. For example, andaliman fruit has antimicrobial activity against a variety of microbial pathogens.[8] Furthermore, it is also an antioxidant with in vitro anti-inflammatory activity, inhibiting the function of tumor necrosis factor and α-interleukin-6 cyclooxygenase.[9]

One of the biggest obstacles to developing andaliman as a functional ingredient is that it is a perishable commodity because of its high moisture content. However, recent scientific findings show a potential reason for its further development in terms of cultivation and processing technology. Several preservation technologies have been proposed to

Table 1. Popular or folkloric uses of *Zanthoxylum* species.

Plant species	Habitat	Folkloric uses
Z. acanthopodium	North Sumatra, Indonesia	Against diarrhea and stomachache, toothache, food preservative, and spice[8,9,28]
Z. alatum	Himalayan region	Cholera, diabetes, cough, diarrhea, fever, headache, microbial infectious, toothache, inflammation, cancer, stomachaic, carminative, disinfectant, antiseptic, fever, dyspepsia, cholera[56,57]
Z. americanum	Canada and North America	Roots, wood, bark and berries: bronchial disease or congestion, burns, cough, itchy skin, pulmonary trouble, ulcerated throat, wounds, or skin sores[6]
Z. armatum	India, China, Taiwan, Nepal, Malaysia, Pakistan	Bark: carminative, stomachic, and anthelmintic. Fruits and seeds: aromatic tonic in fever, dyspepsia, and expelling. Stems: toothache prevention. Leaves and seeds: anti-inflammatory, insecticidal, antifungal, and anti-microbial activities[58–60]
Z. bungeanum	China and Southeast Asia	Pericarp: stomachache, toothache, abdominal pain, ascariosis, diarrhea, dysentery, spices, stimulate saliva, and increase appetite[61–63]
Z. leprieurii	Cameroon	Stomach disorder. Roots and stem bark: gonorrhea, intestinal parasites, and sterility[29]
Z. limonella	Thailand	Stem bark and fruit: stomachache and toothache[64]
Z. nitidium	India, Northern Queensland, Australia	Inflammatory disease, burn pains, cancer, toothache, neuronalgia, stomachache, sore throat, rheumatoid arthritis, turgesence, venomous snake bite[65–67]
Z. piperitum	Japan, Korea, China	Diuretic, abdominal ailment remedy, anthelmintic, and for the treatments of disorder digestive organ[13,68]
Z. rhetsa	India	Fruit and stem bark: treatment of asthma, bronchitis, hearts complaint and rheumatism. Fruit: stimulant, astringent, aromatic, and digestive agent. Essential oil: local anesthetic[30,69]
Z. schinifolium	China, Korea, Japan	Spice and pharmacological uses[70]
Z. syncarpum	North and South America	Leaves: antiparasitic[71]
Z .rhoifolium	Atlantic coast	Anti-inflamatory, infectious processes, and in malaria treatment. Stem bark: flatulence, colic, dyspepsies, earaches, toothaches, and snake bite[72]
Z. zanthoxyloide	Cameroon	Root bark: wounds healing, treatment of intestinal worms, and edema[73]

extend the shelf-life of the raw products (using drying) and derivatives/extracted products (using encapsulation). This review emphasizes recent studies of the plant's flavor profiles, bioactive compounds, and technology used to preserve its valuable chemical compounds. This includes a discussion of encapsulation of andaliman extract to support its development as a functional food flavor ingredient.

Description of andaliman (Z. acanthopodium *DC.*)

Andaliman plant is either a perennial shrub or a low-branching, small tree that grows up to 5 m in height. The plants have thorns on the stems, branches, and twigs. The leaves are scattered and stemmed, ranging from 5 to 20 cm long and 3 to 15 cm wide, and they contain oil glands. The upper surfaces of the leaves are shiny green, and the lower surfaces are light green or pale. Young leaves have green upper surfaces and reddish-green bottoms. Flowers are in the auxiliary and they are small with flat- or conical-shaped bases. The flowers display five to seven free petals 1–2 cm in length. They are a pale yellow color, androgynous, having five to six stamens in the flowers at the base. They have reddish anthers, three to four pistils, and boarded apocarp ovaries. The fruit is box or capsule shaped, or sometimes they are rounded and 2–3 mm diameter.[10] The young fruit is a green color, whereas the mature fruit is red (Fig. 3) with one seed per fruit. The seed possesses a hard skin and shiny black color. Both the green (unripe) and red (ripe) forms can be used as spices. The red ones easily turn into the black form because of ripening. The black one no longer has the typical flavor of andaliman.

Andaliman belongs to family Rutaceae.[11] According to Keng,[11] andaliman is classified as follows:

Division: *Spermatophyta*
Sub division: *Angiospermae*
Class: *Dicotyledoneae*
Order: *Geraniales*
Family: *Rutaceae*
Genus: *Zanthoxylum*
Species: *Zanthoxylum acanthopodium* DC.

The fruit of andaliman is an exotic spice that originated in North Sumatera, Indonesia. It is widely found in Dairi, North Tapanuli, Tobasa, Humbang, Silindung, and Toba Holbung. Its

Figure 3. The fruits of andaliman (*Zanthoxylum acanthopodium* DC.).

habitat is sandy loam soil and it grows at an elevation of 0.9 km above sea level where there can be up to 2500 mm of annual rainfall over 170–180 days of the year.[1] Andaliman is referred to by several names in its native regions, such as sinyar-sinyar (Angkola), intir-intir (Simalungun), toba (Karo), and syarnyar (South Tapanuli).[1]

There are three varieties of andaliman found in North Tapanuli, Tobasa, and Dairi. They are sihorbo, simanuk, and sitanga. Sihorbo has bigger fruit, is less aromatic, and is not produced in large numbers. Simanuk has smaller fruit, a sharper aroma and taste, and a higher production yield. Sitanga has a very strong fruit flavor, but it is less preferred because of its bug aroma.[1] Among these varieties, simanuk is the only one typically sold in the market.

Andaliman is widely consumed by the Batak as a food additive in traditional cuisines and daily food. As a result, it is also known as Bataknese Pepper. The fruit of andaliman, which has a strong and exotic citrus aroma, has been utilized by the local people to mask the fishy flavor of raw fish and the fatty flavor of meat for many years. For example, the Batak community in North Sumatera has a traditional food called naniura, which is made by fermenting raw fish for 24 hours and incorporating andaliman as a spice. This food has the characteristic citrusy and sweet peppery flavor of andaliman.[12]

Some chemical compounds, such as those from chili, onion, pepper, and menthol, can stimulate the trigeminal nerve, causing the perception of burning, heat, pungency, or cold. It can also activate other trigeminal sensations in the mucosa of the eyes, nose, and mouth.[35] In contrast to the spicy sensation of chili or pepper, andaliman also triggers a unique trigeminal sensation called the "biting effect," which is similar to sansho, a well-known Japanese pepper (*Z. piperitum* DC.).[7,13,14] Napitupulu et al.[1] stated that the typical aroma and trigeminal sensation of andaliman are often used to enhance the appetite of a sick person.

The effect of the spiciness of red pepper on the appetite has already studied by Yoshioka et al.[15,16] This research showed that the addition of red pepper to a meal decreases the appetite, as well as the tendency to ingest protein and fat at the next meal in Japanese females. It also influences energy intake in Caucasian males. This effect might be related to an increase in activity of the sympathetic nervous system (SNS) in Caucasian males. These results suggest that the addition of red pepper to the diet decreases energy intake, an effect which might be mediated by an increase in SNS activity.[15] Yoshioka et al.[16] also studied the maximum tolerable dose of red pepper, which can decrease fat intake. They found that a soup with strong spiciness significantly lowers fat intake compared with a placebo, while energy and fat intake are similar after the ingestion of a moderately spicy soup compared with a placebo. Consumption of strong capsules also tends to suppress fat and energy intake, which suggests that the mechanism of action of red pepper does not occur in the mouth. Based upon this research, trigeminal stimulation by andaliman fruit might similarly affect the appetite and food intake. However, further scientific research on the "biting sensation" induced by andaliman is needed.

Flavor profiles

Plants in the genus *Zanthoxylum* are mainly used as spices. Spices derived from *Zanthoxylum* species contain essential oils that have unique flavors. Most of these species have a strong citrus aroma owing to linalool and limonene.[17] *Z. bungeanum* and *Z. schinifolium* have similar aromatic properties.[18] *Z. rhetsa* contains terpinen-4-ol and

alpha terpineol as its primary aromatic compounds.[19] *Z. acanthopodium* contains geranyl acetate and limonene as its aromatic compounds.[12]

There are several methods of aromatic compound extraction, including maceration, headspace, vacuum distillation, and the Likens–Nikerson technique. Different methods of extraction of andaliman flavors produce different aroma profiles.[12] The extracts produced by the Likens–Nickerson and vacuum distillation methods have low-intensity aromas, indicating that the aroma is susceptible to heat. The aroma produced by the Likens–Nickerson method has a lemon peel aroma, whereas the extract produced by vacuum distillation has an andaliman aroma. Meanwhile, extract obtained from the headspace method has a fatty odor, which is very different from the typical fresh andaliman aroma. The extracts obtained by maceration produce a fresh andaliman aroma at a relatively higher intensity.[12]

To optimize the quality of the maceration-derived extract, maceration can be conducted in various types of polar solvents, such as diethyl ether, acetone, chloroform, and ethanol. According to sensory evaluation tests, an extraction using diethyl ether yields extracts with the most representative and intense andaliman aroma.[12] This finding has also been supported by Kojima et al.,[20] who showed that the sansho aroma of *Z. piperitum* can be dissolved more effectively in more highly polar solvent fractions containing oxygenated compounds compared to the hydrocarbon fraction.

The volatile compounds from the extract obtained by maceration are presented in Table 2,[12] and the chromatogram is presented in Fig. 4. Monoterpenes are the main compounds identified, including oxygenated monoterpenes (46.54%) and hydrocarbon monoterpenes (19.75%). The major aromatic compounds (relative peak area >10%) are geranyl acetate (32.04%) and limonene (15.80%). This composition is different from other *Zanthoxylum* plants, such as *Z. piperitum, Z. simulans*, and *Zanthoxylum bungeaman*. In those plants, limonene is found to be the most abundant compound.[21,22] On the other hand, in shansho peels and leaves, geranyl acetate (9.01%) is the third most abundant compound.[23]

From the 30 volatile compounds identified in andaliman, 15 are also present in the Japanese pepper (sansho).[12] These include α-pinene, limonene, (*Z*)-β-ocimene, citronellal, linalool, linalool acetate, caryophyllene, (*E*)-2-decenal, citronelyl acetate, neral, geranial, α-terpineol, geranyl acetate, citronellol, and geraniol. Geranyl acetate (32.04%) is the major compound present in andaliman.

Of all the aromatic compounds, certain ones receive additional attention because they have the biggest effect on the characteristics of the aromas.[24] The key aromatic compounds of andaliman are shown in Table 4.[12] and (Fig. 6).[55] Aroma extract dilution analysis reveals that the potent odorants in andaliman are citronellal (FD [flavor dillution] 128) and limonene (FD = 32) (Fig. 5).[12] These two compounds tended to have the greatest impact on producing the fresh citrus aroma of andaliman. Furthermore, β-myrcene, (*Z*)-β-ocimene, linalool, β-citroneral, geraniol, geranial, an unknown compound, and a sesquiterpene also contribute to andaliman's citrus-like and warm, sweet, peppery aroma. Although geranyl acetate is the major aromatic compound in andaliman, it does not contribute to the flavor of andaliman.[12]

Zanthoxylum species have been known for inducing unique sensations in the mouth. Because of the unique sensation they produce, some of these species have been widely used as food additives and flavorings. *Z. piperitum* has been commercially utilized as a food seasoning in Japan, particularly in a mixture of spices called shichimi togarashi. *Z. simulans*, which is commonly known as the szechuan pepper, has been widely utilized in

Table 2. Volatile compounds of andaliman maceration extract.[12]

No.	Compounds	RI experiment[a]	RI reference[b]	Relative peak area (%)
1	α-Pinene	927	939	0.70
2	β-Myrcene	988	991	2.00
3	Limonene	1028	1021	15.80
4	(*Z*)-β-ocimene	1036	1040	0.39
5	(*E*)-β-ocimene	1046	1050	0.86
6	Linalool	1102	1098	0.76
7	Citronellal	1147	1153	5.63
8	α-Terpineol	1195	1189	0.20
9	β-Citronellol	1234	1228	0.84
10	Neral	1243		0.22
11	Linalool acetate	1253	1240	0.32
12	Geraniol	1260	1257	3.34
13	Geranial	1272	1255	2.57
14	Citronellyl acetate	1351	1270	0.24
15	Geranyl acetate	1386	1354	32.04
16	(*Z*)-β-farnesene	1421	1383	0.51
17	A sesquiterpene	1500	1443	0.13
18	Cubelol	1530		0.19
19	(*Z*)-isoelemicine	1575	1514	0.36
20	A branched alkane	1594	1573	0.21
21	(*Z*)-asarone	1627		9.48
22	(*E*)-asarone	1685	1622	5.86
23	A branched alkane	1792	1679	0.13
24	A terpenyl ester	1839		0.19
25	Unknown	1938		0.53
26	Unknown	1966		0.53
27	Unknown	2063		0.22
28	Unknown	2184		8.67
29	Unknown	2194		0.88
30	Unknown	>2200		6.20

[a]RI experiment from GC–MS, column DB-5.
[b]RI reference by Adams, column DB-5.
Relative peak area was calculated in percentage over the total area of all peaks.
RI: Retention index.

Chinese cuisine. *Z. piperitum* and *Z. acanthopodium* produce a prickling sensation in the mouth and they have a strong, pungent taste.[7] The unique tingling trigeminal sensation of andaliman has also been found to be similar to that of szechuan pepper. However, not all *Zanthoxylum* species cause this kind of tingling sensation. Some *Zanthoxylum* species, such as *Zanthoxylum limonella*, have only a bitter taste, which is elicited by the globular area of the fruit.[25]

According to Wijaya,[7] the tingling sensation in andaliman is due to the presence of (2*E*,6*Z*,8*E*,10*E*)-*N*-(2′methylpropyl)-dodecatetraenamide (Fig. 7) in the fruit pericarp. Bryant and Mezine[26] performed extracellular nerve recordings of the lingual nerve of rats, in addition to human taste-testing on (2*E*,6*Z*,8*E*,10*E*)-*N*-(2-methyl-2-hydroxypropyl)-dodecatetraenamide (hydroxy-α-sanshool), one of the primary compounds in szechuan pepper (*Z. bungeanum*). Based on the human taste-testing, the amide produced a distinct thermal sensation similar to capsaicin. The tingling sensation produced an effect similar to a mild electric shock (5–7 V) and could last 10–20 minutes in the mouth (numbing sensation) following application of 25–50 μg of hydroxy-α-sanshool. Meanwhile, nerve recordings following the application of hidroxy-α-sanshool on the rats' tongues demonstrated that this compound could stimulate seven silent neurons that are not usually stimulated by any other stimuli.

Sugai et al.[27] showed that the burning sensation associated with α-sanshool lasts longer than that of hydroxy-α-sanshool, which indicates that the tingling sensation of the sansho was

Table 3. Scientific research on bioactivity of *Z. acanthopodium* DC.

Bioactivity	Result of the study
Antiradical[28]	Antiradical activity of andaliman extracted with ethanol was higher than hexane and acetone extract. It is also shown by the highest phenolic content of ethanol extract
Antioxidant and antidiabetic[74]	Andaliman extract using ethyl acetate, methanol, and water showed antioxidant activity, in which extract with methanol showed the highest antioxidant activity with IC_{50} value of 390.92 and 30.04 ppm for measurement by DPPH and ABTS method. However, those having activity as α-glucosidase inhibitors were only andaliman extracts using ethyl acetate and methanol, with the highest activity present in methanol extract (IC_{50}: 323 ppm). Fractionation result suggested that the compounds involved in this bioactivity were auron from flavonoid groups and flavonon
Anti-inflammatory[9]	Andaliman extract using ethanol could decrease expression of TNF-α, COX-2, and MMP-9 proteins in macrophages treated with lipopolysaccharide in vitro. At the gene level, andaliman extract blocked the mRNA expression of TNF-α, IL-6, Inos, COX-2, and MMP-9
Antioxidant and cytotoxic activity in breast cancer cells[75]	Crude andaliman extract using petroleum showed weak antioxidant activity. Cytotoxic activity in breast cancer cells T47D had an IC_{50} of 149.4 µg/mL
Antibreast cancer[76]	The inhibitory effect on the growth of T47D breast cancer cells from the combination between ethylacetate extract of andaliman and doxorubicin was higher than the single treatment of doxorubicin. This study suggested that andaliman was potential to be a co-chemotherapeutic for breast cancer. The result of the analysis with flowcytometry show changes in cell accumulation occurring in the G0–G1 cycle
Antibacterial[77]	The extraction of *Z. acanthopodium* by the method of hydrodistilation with Clevenger type apparatus showed the most active inhibition of *S. aureus*
Antibreast cancer[78]	Cytotoxic assay on MCF-7 and T47D breast cancer cells showed andaliman extract using ethyl acetate combined with doxorubucin having the highest activity with IC_{50} values, respectively of 136, 490, and 52.031 µg/mL. Analysis with flowcytometry showed that the mechanism of inhibition of breast cancer cells was not a mechanism of apoptosis. Based on the analysis with TLC, the active compounds found in andaliman extract are alkaloids, flavonoids, and saponins
Antioxidant and antihyperglicemic[79]	Comparison of antioxidant activity and inhibition of α-glucosidase between the andaliman extract and Japanese pepper (*Z. piperitum* DC.) extract showed higher activity found in Japanese pepper extract. However, after undergoing gastrointestinal digestion in vitro, the decline of andaliman extract antioxidant activity was lower by 2.77 times compared to Japanese pepper extract by 8.26 times. This result suggested that antioxidant activity of andaliman extract was more stable compared to Japanese pepper
Anti-aging and *antiacne*[80]	Andaliman extract using ethanol with a concentration of 300 mg/mL showed antibacterial activity against *Propinibacterium acnes* (inhibition area: 15.95 ± 0.46 mm) and *S. aureus* (inhibitory area: 14.61 ± 0.53 mm)

DPPH: 2,2-Diphenyl-1-picrylhydrazyl; ABTS: 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid).

already intense even with the less pungent compound, hydroxyl-α-sanshool. Based on High Performance Liquid Chromatography measurements, andaliman has the highest concentration of α-sanshool, while the Japanese pepper has a higher concentration of hydroxy-α-sanshool (data not shown).

Bioactive compounds

Plants of the genus *Zanthoxylum* are not only used as spices but also as traditional medicines in Asia and North America. Moreover, almost every part of the plant has its own function (Table 1). The leaves and fruits are consumed as a mouth freshener and for tooth care. The bark can help neutralize fish toxin.[8,9] *Zanthoxylum* species, such as *Z.*

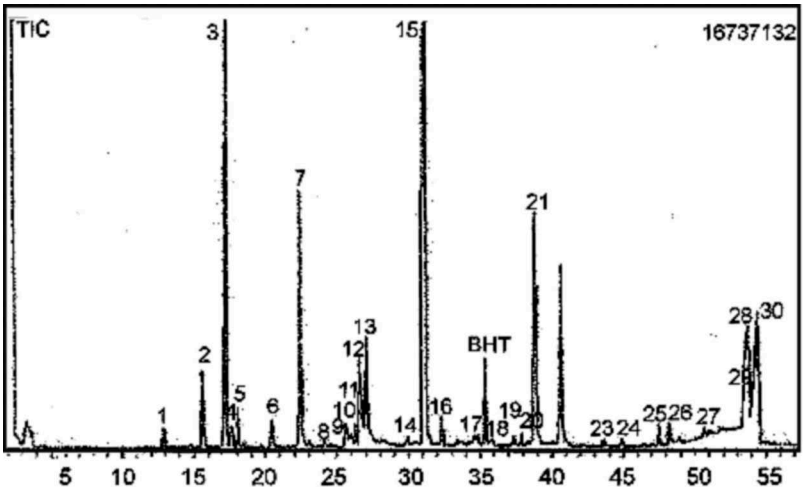

Figure 4. GC–MS chromatogram of andaliman extract obtained by maceration in diethyl ether.[12]

Table 4. Key aroma compounds of Andaliman.[12]

No	RI[a]	RI[b]	RI[c]	Compounds[d]	FD factors	Aroma description
2	985	988	991	β-Myrcene	8	Citrus, sweet, riped
3	1029	1028	1021	Limonene	32	Orange peel, sweet
4	1046	1036	1040	(*Z*)-β-ocimene	4	Citrus, sweet, riped
6	1097	1102	1098	Linalool	8	Citrus, floral
7	1152	1147	1153	Citronellal	128	Citrus, strong, warm
8	1167			Unknown	4	Green
9	1212	1234	1228	β-Citronellol	8	Citrus, warm
10	1227	1243	1240	Neral	8	Lemon, sweet
12	1256	1260	1255	geraniol	4	Floral, citrus aurantifolia leaf
13	1274	1272	1270	Geranial	8	Lemon, sweet
15	1390	1386	1383	Geranyl acetate	4	Citrus, floral, acid
17	1508	1500		A sesquiterpene	4	Woody

[a]RI experiment with GC/O, column HP-5.
[b]RI experiment with GC/MS, column DB-5.
[c]RI reference: Adams, column DB-5.
[d]Aroma compounds stated here are the ones with FD-factor ≥ 4.
FD: Flavor dilution.

piperitum (Japan), *Z. schinifolium* (Korea), *Z. simulans* (Taiwan), and *Z. rhetsa* (India), have been traditionally used in folk medicine to treat toothaches and other types of trigeminal nerve pain. They commonly share a faint lemony taste and numbing sensation, which are different from the intense burning pain associated with hot peppers of the *Capsicum* genus.[28] Moreover, the fruit is also believed to have the ability to enhance the appetite of a sick person.[1]

The *Zanthoxylum* genus contains important alkaloids, viz. benzophenanthridines, furoquinolines, oporphines, which have medicinal uses.[29] Antioxidant and anti-inflammatory compounds have been found in the fruit of some species of *Zanthoxylum*, such as *Z. rhetsa, Z. acanthopodium*, and *Z. piperitum*.[30–32] However, molecular studies of these medicinally important species have rarely been reported.

Zanthoxylum species (Table 1) are commonly used by local societies for ethno-medicinal purposes. Seeds of most *Zanthoxylum* fruits are rich in oil and contain large amounts

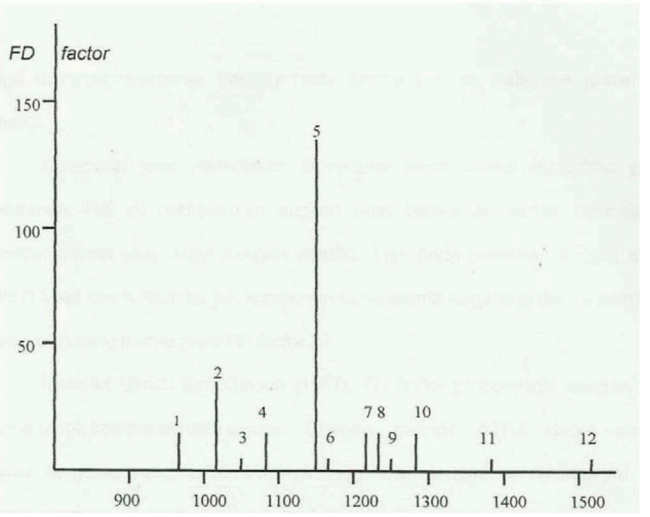

Figure 5. Flavor dilution chromatogram of andaliman.[12]

Figure 6. Key aroma compounds of andaliman (from left to right)[55]: (1) β-myrcene, (2) limonene, (3) (*Z*)-β-ocimene, (4) linalool, (5) citronellal, (6) β-citronellol, (7) neral, (8) geraniol, (9) geranial, (10) geranyl acetate.[55]

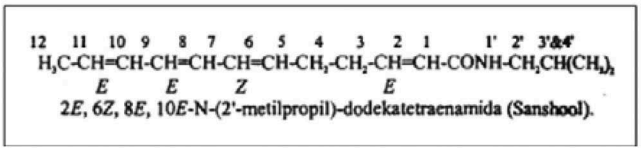
12 11 10 9 8 7 6 5 4 3 2 1 1' 2' 3'&4'
H3C-CH=CH-CH=CH-CH=CH-CH2-CH2-CH=CH-CONH-CH2CH(CH3)2
E E Z E
2E, 6Z, 8E, 10E-N-(2'-metilpropil)-dodekatetraenamida (Sanshool).

Figure 7. Trigeminally active compound of andaliman.[7]

of alkaloids and unsaturated fatty acids, which possess notable antioxidant activities.[32] This probably accounts for several biological activities associated with the *Zanthoxylum* genus, such as anti-inflammatory, analgesic, antinociceptive, antioxidant, antibiotic, hepatoprotective, antiplasmodial, cytotoxic, antiproliferative, anthelminthic, larvicidal, antiviral, and antifungal effects.[29]

Furthermore, some members of the *Zanthoxylum* genus contain a glycoprotein (e.g., Japanese pepper), which may also be present in andaliman. This glycoprotein has been shown to act as an antioxidant and hepatoprotective agent.[32] It has a dose-dependent inhibitory effect on hypoxanthine/xanthine oxidase and glucose/glucose oxidase-induced cytotoxicity. Additionally, Japanese pepper glycoprotein (20 mg/kg) lowers the levels of lactate dehydrogenase, alanine transaminase, and thiobarbituric acid reactive substances, which can enhance the effects of hepatic antioxidant enzymes (superoxide dismutase, catalase, and glutathione peroxidase) in mouse models of carbon tetrachloride-stimulated acute liver injury. The results suggest that the glycoprotein isolated from Japanese peppers can be a potent hepatoprotective agent and a natural antioxidant.[32] Meanwhile, similar activity has also been attributed to andaliman.[31] Kristianti[31] isolated two polar terpenoids from an andaliman *n*-butanol extract. These were 17-((23*E*,26*E*)-23-ethylidene-29-hydroxy-29-(2-hydroxypropoxy)-25-methyldec-26-en-20-yl)-13,15-dimethyl-gona-1,3,5 (10)-trien-3-ol and cholest-5-en-3β-yl β-D-glucopyranoside. These compounds had free radical scavenging potential, which had been investigated in vitro for activity against xanthine oxidase. The IC_{50}s were 0.34 and 0.06 μg/mL, respectively.

There are numerous parts of the *Z. acanthopodium* plant that have been used for traditional folk medicine. Some of andaliman extract bioactivity has been scientifically studied (Table 3). The fruits are used in the treatment of rheumatism, dysentery, and stomach aches.[33] The barks are also used as an aromatic tonic for fevers, dyspepsia, and cholera. The leaves and fruits are used in the treatment of chronic fever, cholera, dyspepsia, dysentery, stomachache, cough, bronchitis, and hair disease.[34] Another research study also showed that andaliman extract has immunostimulatory and antimicrobial activities.[8]

A number of flavone glycosides contained in andaliman have also been reported in various natural sources.[35] Previous phytochemical investigations of the fruits and seeds of andaliman have led to the isolation of herbacetin-7.8.4′-trimethyl ether (tambulin) and 8-*O*-glucosyl-gossypetin-7,4′-dimethyl ether (tambuletin). These fruits have now been reported to have two flavonols, which have been identified as herbacetin-8.4′-dimethyl and a new flavone glycoside.[36] Examination of the dried fruits of *Z. acanthopodium* has led to the isolation of a new flavone glycoside, along with herbacetin-8,4′-dimethyl ether. The new flavone glycoside is 7-*O*-α-D-glycosyl-3,8-dihydroxy-2-(3-hydroxy-4-methoxyphenyl)-5-methoxy-4*H*-1-benzopyran-4-one based on its spectral properties and it is an aglycone.[36]

No further analysis had been done to examine the bioactivity of these isolated compounds in andaliman. However, these compounds are probably the ones responsible for some bioactivities observed for andaliman fruit. For example, 3,5-diacetyltambuline, the flavone glycoside of *Z. integrifoliolum*, is known to have antiplatelet activities.[37] Nine kinds of flavonoids isolated from the leaves of *Zanthoxylum bungeanum* were also found to have strong antioxidant activities.[38] According to an in vivo study by Zhang et al.,[39] flavonoid glycosides of *Polygonum capitatum* have therapeutically protective effects on gastric injuries caused by *Helicobacter pylori*. These results suggest that flavone glycoside, which is a subclass of flavonoid, might have similar bioactivities.

Hashimoto et al.[40] showed that the taste of the active compounds in sansho (β-sanshool, γ-sanshool, and hydroxy-β-sanshool), which were isolated from the pericarp of *Z. piperitum*, affect the gastrointestinal tract. Examination of the muscle in the gastrointestinal tracts of guinea pigs showed that the active compounds act directly upon the gastric muscle, which affects the contractile activities in the ileum and distal colon. A similar amide was also found in andaliman.[7] This work could explain why andaliman is used as a folk medicine for stomach aches.[1] The active compound isolated from andaliman might have a similar effect as that of sansho.

Food technology applications

The most prominent characteristics of andaliman are its flavor profiles and bioactive compounds. However, the flavor and bioactive compounds diminish over long-term storage because of the plant's high moisture content. The decline occurs more rapidly when stored in open conditions at room temperature. These changes are driven by the growth of mold in high relative humidity conditions.[41] The unsaturated aliphatic amide, which is similar to the pungent sanshool compound, is unstable. It has a tendency to be polymerized.[42] Polyunsaturated alkylamides are also not stable and deteriorate easily under UV light and hydrolytic conditions.[18]

Andaliman is subject to fungal decay within 4–5 days after harvest. Over 10–14 days of storage, the color changes to black as it rots. Therefore, proper handling is necessary create a longer shelf-life and preserve the distinctive flavor and biological activities of andaliman. Various processes have been studied to preserve andaliman fruit (i.e., drying, extraction, and encapsulation methods).

A simple method to extend the shelf-life while preserving the flavor of andaliman is drying. Drying is a preservation method that has been widely applied to a variety of spices. There are various methods that can be applied to dry herbs, including exposure to the sun, air, a fluidized bed, oven, far infra-red light, and freeze-drying. However, andaliman contains volatile compounds that are easily degraded by heating. Therefore, this must be considered to minimize the loss of flavor compounds. Drying temperatures and times are critical parameters that need to be controlled carefully.

Napitupulu and Wijaya[43] found that freeze-drying is the best method to preserve andaliman. Considering technical requirements and economic reasons, oven-drying was selected as the appropriate method. Oven-dried andaliman has a moisture content of 5.7% and water activity of 0.49. Moreover, sensory evaluation with multiple comparison tests showed that dried andaliman has a slightly different aroma parameter score compared to fresh andaliman. Based on the optimization study, the suggested oven-drying conditions

are temperatures of 54°C for a drying time of 480 minutes.[43] In addition, Inggita[44] showed that storing dried andaliman in vacuum packaging could maintain a lower moisture content and produce a more intense trigeminal numbing sensation.

The drying process reduces the moisture content to a point where there is not enough water for biological activities or chemical reactions in the cells of the andaliman plant. Although there is a decline in the quality of the flavor of andaliman following drying, it is still acceptable for many months of storage.[43] Additionally, in its dried form, it is easier to transport.

Another method to prolong the shelf-life of andaliman is to preserve it as a concentrated extract or sauce. Ephmara[45] found that the best formula for andaliman sauce contained 5% andaliman and 0.60% citric acid based on the total weight of the sauce. The purpose of citric acid addition is to meet the pH standard of the sauce (pH ≤ 4) and to prevent the loss of the color and aroma. Furthermore, a low pH is necessary to prevent the growth of *Clostrudium botulinum*, which cannot grow below pH 4.5.

Andaliman flavor derives from its essential oils, which are unstable and susceptible to degradation in the presence of oxygen, light, and heat.[7,12] In addition, most essential oils are poorly soluble in water.[46] Therefore, encapsulation can be used to enhance solubility and bioavailability, in addition to controlling the release of the essential oils, which improves overall efficacy.[47] Thus, some attempts have been made to preserve these oils through encapsulation in various colloidal systems, such as microcapsules, microspheres, nanoemulsions, and liposomes.

Encapsulation of andaliman's essential oil via spray-drying has been performed.[48] Andaliman extraction has been achieved using maceration in diethyl ether.[49] Spray-drying encapsulation of andaliman extract was done at an inlet temperature of 150°C with a 1:8 ratio of extract to carrier. The wall materials consisted of maltodextrin and gum arabic in a ratio of 3:2.[48] Quantitative analyses showed that the andaliman powder produced has a flavor similar to fresh andaliman, including a pronounced taste, trigeminal sensation, and citrus-like, sour floral aromas. Wan et al.[50] found that microencapsulation of *Zanthoxylum* essential oil by emulsion inclusion methods using gum arabic, soy protein, maltodextrin, soluble starch, and β-cyclodextrin as the wall material reduces the volatility of the essential oil.

As discussed above, essential oils without encapsulation are unstable and poorly soluble in water. For instance, the essential oil of *Zanthoxylum tingoassuiba* is a complex mixture of organic compounds. Among these, methyl-*N*-methylanthranilate and sesquiterpene alcohol α-bisabolol are poorly soluble in water. This essential oil has antimicrobial activity against dermathophyte fungi and gram-positive bacteria. Encapsulation of essential oil from *Z. tingoassuiba* into dipalmitoylphosphatidylcholine multi-lamellar liposomes has been successfully produced through a thin-film hydration method with a mean diameter of 9.37 ± 4.69 μm.[51] This development of a new antimicrobial formulation shows that encapsulation is a promising method for preserving and increasing the solubility of the essential oil of andaliman fruit.

Beside the development of technology to preserve andaliman as a flavoring ingredient, studies of its function as a natural preservative in food have also been conducted. Tensiska et al.[52] studied the anti-oxidative activities of andaliman as an oil-based preservative. The analysis of antioxidant activity in andaliman extract was performed in three kinds of food systems: the aqueous, emulsion, and oil systems. This research showed that andaliman ethanol and hexane-ethanol extract have the best protective effects in the aqueous system (2 mg of β-

caroten in 10 mL chloroform), which was examined by applying 2 mg of dried andaliman extract. Compared to butylated hydroxytoluene, the protective effects of andaliman extract (200 ppm) in the emulsion and oil systems are less. However, these still have moderate activity because the flavonoid and polyphenolic compounds are less dissolved in oil- and fat-based systems. However, the stability during heating is relatively good. In the aqueous system, heating treatment at a temperature of 170°C for 120 minutes reduced the protective effects by about 17% for the ethanol extract and 13% for the hexane–ethanol extract.

Andaliman has also been reported for its strong antimicrobial activity. Parhusip[53] found that andaliman extracted using ethyl acetate more effectively inhibits *Bacillus cereus, Staphylococcus aureus*, and *Salmonella typhimurium* compared to the extraction method using methanol and hexane. A concentration of 50% (w/w) ethyl acetate extract could produce 31.6, 27.1, and 33.4 mm inhibition activity during the log phase of *B. cereus, S. aureus*, and *S. typhimurium*, respectively. An additional study showed that andaliman extract increases the permeability and hydrophobicity of the cell membrane of *B. cereus*. Phenolic compounds contained in andaliman extract likely interact with the cytoplasmic membrane to increase its permeability.[8] This research suggests a mechanism by which andaliman acts as a natural preservative to prevent the growth of harmful pathogen bacteria.

Conclusion and future outlook

Andaliman (*Z. acanthopodium* DC.) is a plant endemic to Indonesia. This plant belongs to the genus *Zanthoxylum* and is commonly used as a spice. The fruit possesses unique flavor properties and bioactive compounds. Monoterpenes are the main compounds among those identified in andaliman, and oxygenated monoterpenes are the major constituents (46.54%), followed by hydrocarbon monoterpenes (19.75%). The primary volatile compounds in andaliman (relative peak area >10%) are geranyl acetate (32.04%) and limonene (15.80%); however, citronellal and limonene are determined as key aromatic compounds based on GC–O measurements. Andaliman also contains amides, which are responsible for the unique tingling sensation that andaliman induces. Beside the aliphatic acid amides, andaliman fruits and leaves contain terpenoids, alkaloids, flavonoids, and other phenolics, which can function as antioxidants.[54]

The genus *Zanthoxylum* may be considered to be an emerging spice. These spices can have both health benefits and unique flavors. Further study is needed to develop scientific evidence to support traditional claims. This effort is important for the future use of andaliman because only a few studies have been conducted thus far. Preservation technology research is also needed to make andaliman more useful. This species has many potential benefits as a plant-based flavoring agent and applications in the pharmaceutical industry in the future.

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